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# Theory of Mössbauer line broadening due to diffusion of Mössbauer atoms via vacancies

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We have calculated analytically the effect of diffusion on the Mössbauer line, especially considering the correlation effects due to diffusion via vacancies. Starting from a hierarchy of rate equations for single-particle densities, pair correlation functions, and higher-order correlation functions we have deduced for small vacancy concentrations an effective equation for the motion of Mössbauer atoms which is similar to the well-known "encounter model". The transport of Mössbauer atoms is described by an effective jump-frequency matrix which incorporates the temporal and spatial correlations of the atomic jumps induced by a single vacancy. We calculate the effective jump-frequency matrix analytically by an iteration with respect to the number of atomic jumps during an encounter. It turns out that the correlation of the atomic jumps diminishes the diffusion broadening of the Mössbauer line. This eliminates some of the discrepancies between Mössbauer studies and radio-tracer experiments.

## I. INTRODUCTION

The Mössbauer effect provides a possibility to study diffusion in solids on a microscopic scale in space and time.[1] Due to diffusional motion of Mössbauer atoms, the Mössbauer line is broadened. From the width one can deduce the atomic jump frequency. Thus the Mössbauer technique is a supplementary method to the standard tracer technique. However, to interprete the results obtained with Mössbauer spectroscopy one has to describe the motion of the atoms microscopically, which has not been done until recently. Thus discrepancies were found when the results of the two methods were compared.[2-6] Knauer[7] and Krivoglaz and Repetsky[8] have first discussed the influence of correlation on Mössbauer line broadening. More recently the diffusional jumps of a substitutional Mössbauer atom via vacancies, and the resulting correlation effects have been considered in detail by Dibar-Ure and Flinn[9,10] using numerical methods, and by Wolf[11] who applied his theory developed for NMR to Mössbauer spectroscopy. In the present paper, which is a condensed version of our earlier report,[12] we present an analytical calculation of the influence of diffusion of Mössbauer atoms on the Mössbauer line. We restrict our treatment to self-diffusion, i.e., we do not take into account any disturbance of the vacancy jumps in the neighborhood of Mössbauer atoms. The effects of changed vacancy jump rates have been considered to some extent by Knauer[7] and by Krivoglaz and Repetsky.[8]

According to Singwi and Sjölander[1] the emission probability of $\gamma$ rays from a Mössbauer atom is proportional to the scattering function $S(\vec{k},\omega)$ which characterizes the motion of the atom. If the vibrational and diffusional dynamics of the Mössbauer atom can be separated, i.e., if the jump frequency is much less than the characteristic vibrational frequencies, one need only consider the diffusional motion. Vibrations give rise to a decrease of the intensity of the Mössbauer line by a Debye-Waller factor. The diffusional part of the scattering function is given by

$$S(\vec{k},\omega)=\int_0^\infty dt\,\tfrac{1}{4}\gamma e^{-\gamma t/2}(e^{-i\omega t}+e^{i\omega t}) \times \sum_{\vec{n}} e^{-i\vec{k}\cdot\vec{R}^{\vec{n}}}G_M(\vec{n},t)\ , \tag{1.1}$$

with $\int d\omega\, S(\vec{k},\omega)=\pi\frac{1}{2}\gamma$. Here $\vec{k}$ is the wave vector of the photon which is related to the energy $\hbar\omega_{\vec{k}}$ of Mössbauer radiation by $\hbar\omega_{\vec{k}}=\hbar c|\vec{k}|$, $\hbar\omega=\hbar(\omega_0-\omega_{\vec{k}})$ is the energy transfer to the system. If $\omega=0$ the emitted photon is elastically scattered and carries the total energy $\hbar\omega_0$, which is the difference between the energies of the excited nuclear state and the ground state. $\gamma$ is the natural linewidth, i.e., $\gamma^{-1}$ is the mean lifetime of the excited state. $G_M(\vec{n},t)$ is the diffusional Green's function of the Mössbauer atom which depends on the discrete lattice site $\vec{R}^{\vec{n}}$ and the time $t$. It gives the probability to find a Mössbauer atom at time $t$ at the site $\vec{R}^{\vec{n}}$ if it started at the site $\vec{R}=0$ at time $t=0$.

In order to discuss the effect of atomic diffusion on the Mössbauer line one has to calculate the Green's function of the Mössbauer atom. Singwi and

Sjölander[1] have solved the problem for an uncorrelated diffusion mechanism, i.e., if the atomic jump probabilities do not depend on the direction of previous jumps. The only diffusion mechanism for which this is true is the direct interstitial diffusion.[13] The uncorrelated motion of atoms can be described by a simple rate equation and the resulting Mössbauer line is a broadened Lorentzian[1]

$$S(\vec{k},\omega)=\frac{1}{2}\gamma\frac{\frac{1}{2}\gamma+\bar{\Lambda}(\vec{k})}{[\frac{1}{2}\gamma+\bar{\Lambda}(\vec{k})]^2+\omega^2} \quad . \tag{1.2}$$

For a nearest-neighbor jump model, the diffusional broadening $\bar{\Lambda}(\vec{k})$ is given by

$$\bar{\Lambda}(\vec{k})=Z\Gamma_M-\Gamma_M\sum_{\vec{l}}{}'\cos\vec{k}\cdot\vec{R}^{\vec{l}} \quad , \tag{1.3}$$

where $\Gamma_M$ is the (uncorrelated) jump frequency of an atom and $\vec{R}^{\vec{l}}$ are interstitial sites; the summation is over nearest-neighbor sites only. $Z$ is the number of nearest neighbors. The broadening (1.3) strongly depends on the direction of the $\gamma$-ray emission relative to the crystal axes.

Usually, Mössbauer atoms occupy regular lattice sites and diffuse via vacancies. Due to this mechanism correlation effects arise, i.e., successive jumps of a Mössbauer atom are no longer independent in space and time. Correlation effects are discussed in detail in the book of Manning.[13]

In early interpretations of Mössbauer line-broadening correlation effects were taken into account by merely scaling the atomic jump frequency with the macroscopic correlation factor. This is not correct as we will show in the following. In Sec. II.A we describe the motion of a Mössbauer atom with a single vacancy, and use an iteration procedure with respect to the number of atomic jumps to calculate the distribution of the Mössbauer atom. Then in Sec. II.B we deal with the diffusion of Mössbauer atoms in the presence of many vacancies. In Sec. III. we calculate the resulting Mössbauer line shape. It turns out that in the case of self-diffusion (unaltered vacancy jump frequencies) temporal correlations have no measurable effect on the Mössbauer line shape, (this is shown in detail in the Appendix). In Sec. IV. we compare our analytical results with earlier calculations and with experiments.

## II. DIFFUSION OF SUBSTITUTIONAL MÖSSBAUER ATOMS

Substitutional Mössbauer atoms can diffuse through the lattice at high temperatures when the concentration and jump frequency of vacancies is sufficiently large. The Mössbauer line is influenced by the dynamics of Mössbauer atoms on a microscopic scale in space and time. Thus we have to describe the diffusional motion of the atoms in detail. We first treat the local motion due to jumps with a single vacancy and then the macroscopic diffusion in the presence of many vacancies. We shall consider the case of self-diffusion only, i.e., we do not take into account changes of the vacancy jump frequencies in the neighborhood of Mössbauer atoms.

### A. Dynamics of a Mössbauer atom with a single vacancy

#### *1. Green's functions*

We define the pair-correlation function $W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}')$, which is the joint probability, to find the Mössbauer atom at the lattice site $\vec{R}^{\vec{n}}$ and the vacancy at $\vec{R}^{\vec{m}}$ at time $t$, if at time $t=0$ the atom was at $\vec{R}^{\vec{n}'}$ and the vacancy at $\vec{R}^{\vec{m}'}$. Since the atom and the vacancy must occupy different sites we have

$$W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{n}')=0=W(\vec{n}\vec{n},t\,|\,\vec{n}'\vec{m}') \quad .$$

The normalization is

$$\sum_{\vec{n},\vec{m}}W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}')=(1-\delta_{\vec{n}',\vec{m}'})\Theta(t)$$

with

$$\Theta(t)=\begin{cases}0, & t<0\\ 1, & t>0\end{cases} \tag{2.1}$$

From the microscopic reversibility of the elementary jump process follows the relation

$$W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}')=W(\vec{n}'\vec{m}',t\,|\,\vec{n}\vec{m}) \quad . \tag{2.2}$$

This means that the same number of paths leads from starting points $(\vec{n}'\vec{m}')$ to end points $(\vec{n}\vec{m})$ as if starting and end points were interchanged. If only nearest-neighbor jumps are considered, the pair-correlation function obeys the following rate equation:

$$\begin{aligned}\dot{W}(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}') ={}& \Gamma_V s_{\vec{n}-\vec{m}}[W(\vec{m}\vec{n},t\,|\,\vec{n}'\vec{m}')-W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}')]+(1-\delta_{\vec{n}\vec{m}})\\ &\times\sum_{\vec{m}''}(1-\delta_{\vec{n}\vec{m}''})\Gamma_V s_{\vec{m}-\vec{m}''}[W(\vec{n}\vec{m}'',t\,|\,\vec{n}'\vec{m}')-W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}')]\\ &+\delta(t)\,\delta_{\vec{n}\vec{n}'}\delta_{\vec{m}\vec{m}'}(1-\delta_{\vec{n}'\vec{m}'})\end{aligned} \tag{2.3}$$

with

$$s_{\vec{n}-\vec{m}}=\begin{cases}1, & \text{if } \vec{n} \text{ and } \vec{m} \text{ are nearest neighbors}\\ 0, & \text{otherwise}\end{cases} \tag{2.4}$$

$$\sum_{\vec{n}} s_{\vec{n}-\vec{m}}=Z\ .$$

$\Gamma_V$ is the vacancy jump rate and $Z$ is the number of nearest neighbors. The first term on the right-hand side of Eq. (2.3) describes the exchange of sites of Mössbauer atom and vacancy; the second term describes the free diffusion of the vacancy in the lattice without passing the site $\vec{n}$ of the atom. The production of atom and vacancy at time $t=0$ is given by the last term. Because we assume a homogeneous crystal, it is always possible to choose one starting point, say $\vec{n}'$, to be the origin.

From the pair-correlation function we can get the distribution function for the atom or the vacancy alone. If we sum over $\vec{n}$ we find the vacancy distribution function $G_V$, i.e.,

$$\begin{aligned}\sum_{\vec{n}} W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}') &= G_V(\vec{m},t\,|\,\vec{n}'\vec{m}')\\ &= G_V(\vec{m},t\,|\,\vec{m}')(1-\delta_{\vec{n}'\vec{m}'})\ ,\end{aligned} \tag{2.5}$$

with the normalization $\sum_{\vec{m}} G_V(\vec{m},t\,|\,\vec{m}')=\Theta(t)$. The probability $G_V(\vec{m},t\,|\,\vec{m}')=G_V(\vec{m}-\vec{m}',t)$, to find the vacancy for $t>0$ at $\vec{m}$, if it was produced at $\vec{m}'$ at $t=0$, obeys the following equation:

$$\begin{aligned}\dot{G}_V(\vec{m}-\vec{m}',t) &= \sum_{\vec{m}''}\Gamma_V s_{\vec{m}-\vec{m}''}[G_V(\vec{m}''-\vec{m}',t)-G_V(\vec{m}-\vec{m}',t)]+\delta(t)\delta_{\vec{m},\vec{m}'}\\ &= -\sum_{\vec{m}''}\Lambda(\vec{m}-\vec{m}'')G_V(\vec{m}''-\vec{m}',t)+\delta(t)\delta_{\vec{m},\vec{m}'}\ .\end{aligned} \tag{2.6}$$

Here the nearest-neighbor jumps are described by the jump matrix $\Lambda$, i.e.,

$$\Lambda(\vec{m}-\vec{m}'')=-\Gamma_V s_{\vec{m}-\vec{m}''}+\delta_{\vec{m},\vec{m}''}\sum_{\vec{l}}\Gamma_V s_{\vec{m}-\vec{l}}\ . \tag{2.7}$$

$\Lambda$ is translational invariant and we have $\sum_{\vec{m}\text{ or }\vec{m}''}\Lambda(\vec{m}-\vec{m}'')=0$. Equation (2.6) can be solved by Fourier transformation in space and time. One obtains

$$G_V(\vec{m},t)=\int\frac{d\omega}{2\pi}e^{-i\omega t}\int_{V_B}\frac{d\vec{k}}{V_B}e^{i\vec{k}\cdot\vec{R}^{\vec{m}}}\hat{G}_V(\vec{k},\omega) \tag{2.8}$$

with

$$\begin{aligned}\hat{G}_V(\vec{k},\omega) &= \int dt\, e^{i\omega t}\sum_{\vec{m}} e^{-i\vec{k}\cdot\vec{R}^{\vec{m}}}G_V(\vec{m},t)\\ &= \frac{1}{-i\omega+\tilde{\Lambda}(\vec{k})}\ ,\end{aligned} \tag{2.9}$$

$$\tilde{\Lambda}(\vec{k})=\sum_{\vec{m}}\Gamma_V s_{(\vec{m})}(1-\cos\vec{k}\cdot\vec{R}^{\vec{m}})\ . \tag{2.10}$$

The second integral in Eq. (2.8) is taken over the first Brillouin zone with $V_B=(2\pi)^3/V_{\text{at}}$; $V_{\text{at}}$ is the atomic volume.

In the following we need the frequency transformed function $\tilde{G}_V(\vec{m}-\vec{m}',\omega)$ of $G_V(\vec{m}-\vec{m}',t)$. From Eq. (2.6) follows:

$$(-i\omega)\tilde{G}_V(\vec{m}-\vec{m}',\omega)=\sum_{\vec{m}''}\Gamma_V s_{\vec{m}-\vec{m}''}[\tilde{G}_V(\vec{m}''-\vec{m}',\omega)-\tilde{G}_V(\vec{m}-\vec{m}',\omega)]+\delta_{\vec{m},\vec{m}'} \tag{2.11}$$

with the normalization

$$\sum_{\vec{m}}\tilde{G}_V(\vec{m}-\vec{m}',\omega)=\frac{1}{-i\omega}\ . \tag{2.12}$$

The summation over the vacancy sites in the pair-correlation function leads to the distribution function $T_M$ for the Mössbauer atom, i.e.,

$$\begin{aligned}\sum_{\vec{m}} W(\vec{n}\vec{m},t\,|\,\vec{n}'\vec{m}') &= T_M(\vec{n},t\,|\,\vec{n}'\vec{m}')\\ &= \sum_{\vec{m}} W(\vec{n}'\vec{m}',t\,|\,\vec{n}\vec{m})\ .\end{aligned} \tag{2.13}$$

The last equation follows from the relation (2.2). From Eq. (2.3) we can obtain a rate equation for the distribution function $T_M$. Rather than solving this we will calculate the pair-correlation function $W$ from Eq. (2.3), and calculate $T_M$ via Eq. (2.13).

In the pair-correlation function $W$, the motion of the Mössbauer atom is coupled to that of the vacancy. After the first exchange, the vacancy is located on a nearest-neighbor site. The atom can jump once more only if the vacancy returns to the site of the atom. We call $R$ the probability of return of the vacancy. Then $1-R$ is the probability that the vacancy will escape from a nearest-neighbor position without passing the site of the atom. If the vacancy returns once (probability $R$) and causes another jump of the atom, then it starts again from a nearest-neighbor position. The situation is the same as before: either the vacancy leaves (probability $1-R$) or it induces a further jump of the atom. Therefore the probability for exactly two jumps of the atom with the same vacancy (the first exchange and one return of the vacancy) is $R(1-R)$. In general the probability for exactly $p$ returns is

$$w(p)=R^{p}(1-R)\ . \tag{2.14}$$

The distribution is normalized, $\sum_{p=0}^{\infty} w(p)=1$. The average number of vacancy returns is

$$\bar{p}=\sum_{p} p\,w(p)=\frac{R}{1-R}\ , \tag{2.15}$$

and thus the average number of jumps of a Mössbauer atom with one vacancy is

$$\bar{j}=1+\bar{p}=\frac{1}{1-R}\ . \tag{2.16}$$

We will see in Sec. III. that in three-dimensional lattices, $R$ is much smaller than one (in cubic lattices $R<0.35$). Then also $\bar{p}$ is small compared to unity and because of the exponential decrease of the return probability the Mössbauer atom will only make very few jumps with the same vacancy (The average number of jumps in the cubic lattices is $\bar{j}<1.54$). So one can calculate the distribution function of the Mössbauer atom using an iteration with respect to the number of atomic jumps. A good approximation for the distribution function can be obtained by taking into account only a few jumps. We deal with the iteration procedure in Sec. II.A 3. Because of the small number of jumps the Mössbauer atom will, with large probability, remain near its starting point after an encounter with one vacancy. Thus many vacancies are needed for its macroscopic diffusion; we treat this problem in Sec. II. B.

### 2. *Return probability and vacancy diffusion with absorption*

We want to calculate the probability of one return of the vacancy of the Mössbauer atom at site $\vec{n}$. The probability that the vacancy returns from a nearest-neighbor position with the next jump to the site of the atom is $Z^{-1}$, with $Z$ the number of nearest neighbors. But the vacancy can first leave the neighborhood of the atom. Then there are contributions to the return probability from all paths through the lattice that lead the vacancy back to $\vec{n}$. The vacancy starting at a neighbor site $\vec{m}$ of the atom can diffuse freely over all lattice sites except $\vec{n}$, the site of the atom. This exclusion of $\vec{n}$ can be described by an absorption condition at $\vec{n}$, which guarantees that the vacancy once it has reached $\vec{n}$, does not jump back into the rest of the lattice. The return probability is then given by the probability that the vacancy is absorbed at $\vec{n}$ if it started at a nearest-neighbor site of $\vec{n}$.

In order to describe the vacancy motion with absorption we define the Green's function $F_{\vec{n}}(\vec{m},t\,|\,\vec{m}\,')$. It is the probability of finding a vacancy at site $\vec{m}$ for $t>0$, which was produced at $\vec{m}\,'$, at time $t=0$, if it can be absorbed at $\vec{n}$. $F_{\vec{n}}$ is different from the ideal vacancy Green's function $G_V$ due to the absorption condition at $\vec{n}$, i.e.,

$$F_{\vec{n}}(\vec{n},t\,|\,\vec{m}\,')=0\ . \tag{2.17}$$

The equation of motion reads

$$\dot{F}_{\vec{n}}(\vec{m},t\,|\,\vec{m}\,')=\sum_{\vec{m}\,''}\Gamma_V s_{\vec{m}-\vec{m}\,''}[F_{\vec{n}}(\vec{m}\,'',t\,|\,\vec{m}\,')-F_{\vec{n}}(\vec{m},t\,|\,\vec{m}\,')]-\delta_{\vec{n},\vec{m}}A_{\vec{n}}^{\vec{m}\,'}(t)+\delta(t)\,\delta_{\vec{m}\vec{m}\,'}(1-\delta_{\vec{m}\,'\vec{n}})\ . \tag{2.18}$$

The terms in the sum describe the free diffusion of the vacancy. For $\vec{n}=\vec{m}$ the additional negative term $A_{\vec{n}}^{\vec{m}\,'}(t)$ is the rate of absorption, i.e., the rate with which the vacancy jumps to the site $\vec{n}$

$$A_{\vec{n}}^{\vec{m}\,'}(t)=\sum_{\vec{m}\,''}\Gamma_V s_{\vec{s}-\vec{m}\,''}F_{\vec{n}}(\vec{m}\,'',t\,|\,\vec{m}\,')\ . \tag{2.19}$$

The return probability per unit time from a nearest-neighbor site is given by

$$\alpha(t)=A_{\vec{n}}^{\vec{m}\,'}(t)\,s_{\vec{n}-\vec{m}\,'}\ , \tag{2.20}$$

and by integration over time we find $R$

$$\begin{aligned}R&=\int_0^{\infty}\alpha(t)\,dt\\&=\int_0^{\infty}\sum_{\vec{m}\,''}\Gamma_V s_{\vec{n}-\vec{m}\,''}F_{\vec{n}}(\vec{m}\,'',t\,|\,\vec{m}\,')\,s_{\vec{n}-\vec{m}\,'}\,dt\ .\end{aligned} \tag{2.21}$$

To calculate $R$ we solve Eq. (2.18) with the ideal Green's function $G_V$ yielding

$$\begin{aligned}F_{\vec{n}}(\vec{m},t\,|\,\vec{m}\,')=&\ G_V(\vec{m}-\vec{m}\,',t)(1-\delta_{\vec{m}\,',\vec{n}})\\&-\int_0^{\infty}\sum_{\vec{m}\,''}G_V(\vec{m}-\vec{m}\,'',t-t')\\&\times\delta_{\vec{m}\,''\vec{n}}A_{\vec{n}}^{\vec{m}\,'}(t')\,dt'\ .\end{aligned} \tag{2.22}$$

$A_{\vec{n}}^{\vec{m}'}(t)$ is determined by the absorption condition, Eq. (2.17). Using a Fourier transformation we obtain

$$\tilde{A}_{\vec{n}}^{\vec{m}'}(\omega) = \frac{\tilde{G}_V(\vec{n}-\vec{m}',\omega)}{\tilde{G}_V(0,\omega)}(1-\delta_{\vec{m}',\vec{n}}) \quad . \tag{2.23}$$

By inserting into the Fourier-transformed Eq. (2.22) we get

$$\tilde{F}_{\vec{n}}(\vec{m},\omega|\vec{m}') = \left(\tilde{G}_V(\vec{m}-\vec{m}',\omega) - \tilde{G}_V(\vec{m}-\vec{n},\omega) \times \frac{\tilde{G}_V(\vec{n}-\vec{m}',\omega)}{\tilde{G}_V(0,\omega)}\right)(1-\delta_{\vec{m}',\vec{n}}) \quad . \tag{2.24}$$

For $\vec{n}$ and $\vec{m}'$ nearest-neighbor sites, we find from Eq. (2.20),

$$\tilde{\alpha}(\omega) = \tilde{G}_V(N_1,\omega)/\tilde{G}_V(0,\omega) \quad . \tag{2.25}$$

Here $\tilde{G}_V(N_1,\omega)$ is the Green's function for a nearest-neighbor site. The return probability, which is the integral over time of $\alpha(t)$, is given by the stationary limit $\omega=0$ of $\tilde{\alpha}(\omega)$, i.e.,

$$R = \tilde{\alpha}(\omega=0) = g_V(N_1)/g_V(0) \quad , \tag{2.26}$$

with the stationary Green's function

$$g_V(\vec{m}) = \tilde{G}_V(\vec{m},\omega=0) = \int_0^\infty G_V(\vec{m},t)\,dt \quad .$$

This is the solution of the stationary equation of motion [compare Eq. (2.6)]

$$0 = \sum_{\vec{m}''} \Gamma_V s_{\vec{m}-\vec{m}''}[g_V(\vec{m}''-\vec{m}') - g_V(\vec{m}-\vec{m}')] + \delta_{\vec{m},\vec{m}'} \quad . \tag{2.27}$$

Especially for $g_V(0)$, i.e, $\vec{m}=\vec{m}'$, we obtain $Z\Gamma_V g_V(0) = Z\Gamma_V g(N_1)+1$. Now we find for $R$

$$R = 1 - \frac{1}{Z\Gamma_V g(0)} \quad . \tag{2.28}$$

The numerical values of the stationary Green's functions are listed, e.g., in Ref. 12. For cubic lattices we compute[14,15] the following values for $R$: sc, $R=0.3405$; bcc, $R=0.2822$; fcc, $R=0.2563$.

### 3. *Iteration procedure*

As discussed in Sec. II.A we want to calculate the pair-correlation function by an iteration procedure with respect to the number of jumps of the Mössbauer atom. This is possible with help of the Green's function $F_{\vec{n}}$ because it allows us to specify the number of returns to a fixed lattice site $\vec{n}$, which we identify with the site of the Mössbauer atom. Each return of the vacancy induces one jump of the atom. The general solution of Eq. (2.3) is given by the integral equation

$$W(\vec{n}\vec{m},t|\vec{n}'\vec{m}') = \delta_{\vec{n},\vec{n}'}F_{\vec{n}}(\vec{m},t|\vec{m}') + \int_0^t dt' \sum_{\vec{m}''} F_{\vec{n}}(\vec{m},t-t'|\vec{m}'')\Gamma_V s_{\vec{n}-\vec{m}''} W(\vec{m}''\vec{n},t'|\vec{n}'\vec{m}') \quad . \tag{2.29}$$

The first term on the right describes the distribution of the atom-vacancy pair, if the vacancy does not visit the atomic site and therefore the atom makes no jump. The second term contains all changes of sites of the atom with the vacancy. It has the following structure:

$$\Gamma_V s_{\vec{n}-\vec{m}''} W(\vec{m}''\vec{n},t'|\vec{n}'\vec{m}')\,dt'$$

is the rate, with which at time $t'$ atom and vacancy change sites during the time interval $dt'$, such that the vacancy arrives at $\vec{m}''$ and the atom at $\vec{n}$. This means that the atom jumps at least once. In the remaining time $t-t'$ the vacancy migrates from $\vec{m}''$ to $\vec{m}$ without passing the site of the atom again. Because the last jump of the atom can happen at any time $t'<t$, we have to integrate over $t'$.

Now we obtain an expansion of the distribution function with respect to the number of atomic jumps by iterating the solution, Eq. (2.29), i.e.,

$$W^{(0)}(\vec{n}\vec{m},t|\vec{n}'\vec{m}') = \delta_{\vec{n},\vec{n}'}F_{\vec{n}}(\vec{m},t|\vec{m}') \tag{2.30}$$

is the contribution to the distribution function, if the atom does not jump.

$$W^{(1)}(\vec{n}\vec{m},t|\vec{n}'\vec{m}') = \int_0^t dt' \sum_{\vec{m}''} F_{\vec{n}}(\vec{m},t-t'|\vec{m}'')\Gamma_V s_{\vec{n}-\vec{m}''} W^{(0)}(\vec{m}''\vec{n},t'|\vec{n}'\vec{m}') \tag{2.31}$$

is the contribution of just one atomic jump. In general the contribution of exactly $\nu+1$ jumps is

$$W^{(\nu+1)}(\vec{n}\vec{m},t|\vec{n}'\vec{m}') = \int_0^t dt' \sum_{\vec{m}''} F_{\vec{n}}(\vec{m},t-t'|\vec{m}'')\Gamma_V s_{\vec{n}-\vec{m}''} W^{(\nu)}(\vec{m}''\vec{n},t'|\vec{n}'\vec{m}') \quad . \tag{2.32}$$

The complete distribution is given by the sum

$$W(\vec{n}\vec{m},t|\vec{n}'\vec{m}')=\sum_{\nu=0}^{\infty}W^{(\nu)}(\vec{n}\vec{m},t|\vec{n}'\vec{m}') \ . \tag{2.33}$$

The pair-correlation function is normalized to unity [$t>0,\vec{n}'\neq\vec{m}'$, see Eq. (2.1)]. We can use this condition to check the quality of the approximation: taking into account $\nu$ jumps the norm is fulfilled to terms of the order of $R^{\nu+1}$ for $t\to\infty$; for a finite time interval $R$ is replaced by the return probability until time $t$, $\int_0^t\alpha(t')\,dt'$.

Later we will need the Fourier transform $\tilde{W}_\mu(\omega)$ of the distribution function $W_\mu(t)$ after $\mu$ jumps, i.e.,

$$W_\mu(\vec{n}\vec{m},t|\vec{n}'\vec{m}')=\sum_{\nu=0}^{\mu}W^{(\nu)}(\vec{n}\vec{m},t|\vec{n}'\vec{m}') \ .$$

For $\mu=0$ and $\mu=1$ this reads

$$\tilde{W}_0(\vec{n}\vec{m},\omega|\vec{n}'\vec{m}')=\delta_{\vec{n},\vec{n}'}\tilde{F}_{\vec{n}}(\vec{m},\omega|\vec{m}') \ , \tag{2.34}$$

$$\tilde{W}_1(\vec{n}\vec{m},\omega|\vec{n}'\vec{m}')=\delta_{\vec{n},\vec{n}'}\tilde{F}_{\vec{n}}(\vec{m},\omega|\vec{m}')+\tilde{F}_{\vec{n}}(\vec{m},\omega|\vec{n}')\,\Gamma_V s_{\vec{n}-\vec{n}'}\tilde{F}_{\vec{n}'}(\vec{n},\omega|\vec{m}') \ . \tag{2.35}$$

### B. Dynamics of the Mössbauer atom with many vacancies

Since the Mössbauer atom only makes a few jumps with one vacancy, a long-ranged diffusion can only be achieved by encounters with many vacancies. The vacancy density $c_V$ in metals is typically smaller than $10^{-4}$. Thus the probability that two vacancies are in the neighborhood of the atom at the same time, which is proportional to $c_V^2$ is very small and these configurations can be neglected. Then the atomic motion can be considered as consisting of successive independent encounters with vacancies. This well-known "encounter model" has already been used by several authors[16,17] to describe diffusion of atoms by the vacancy mechanism. We will deduce this approximation for the atomic motion formally starting with a system of equations for correlation functions of the atom with many vacancies.

#### 1. *Equations of motion*

For the scattering function Eq. (1.1) we need the probability $G_M(\vec{n},t)$ to find the Mössbauer atom at the lattice site $\vec{n}$ at time $t>0$, if it was produced at $\vec{n}'$ at $t=0$. This probability is normalized to unity for $t>0$, i.e., $\sum_{\vec{n}}G_M(\vec{n},t)=\Theta(t)$. The diffusion equation reads

$$\dot{G}_M(\vec{n},t)=\sum_{\vec{m}}\Gamma_V s_{\vec{n}-\vec{m}}[G_2(\vec{m}\vec{n},t)-G_2(\vec{n}\vec{m},t)]+\delta(t)\delta_{\vec{n},0} \ . \tag{2.36}$$

Here $G_2$ is the density of atom-vacancy pairs: it gives the average number of pairs with a Mössbauer atom at $\vec{n}$ and a vacancy at $\vec{m}$. $G_M(\vec{n},t)$ changes in time because of atom-vacancy exchanges, it decreases by jumps of the atom to neighbor sites $\vec{m}$ and it increases, if the atom reaches $\vec{n}$. $\delta(t)\delta_{\vec{n},0}$ is the production term for the atom.

The pair density $G_2$ is normalized to $\sum_{\vec{m}}G_2(\vec{n}\vec{m},t)=N_VG_M(\vec{n},t)$. It is determined by the equation

$$\dot{G}_2(\vec{n}\vec{m},t)=\Gamma_V s_{\vec{n}-\vec{m}}[G_2(\vec{m}\vec{n},t)-G_2(\vec{n}\vec{m},t)]+(1-\delta_{\vec{n},\vec{m}})\sum_{\vec{m}''}(1-\delta_{\vec{n},\vec{m}''})\Gamma_V s_{\vec{m}-\vec{m}''}\,[G_2(\vec{n}\vec{m}'',t)-G_2(\vec{n}\vec{m},t)]$$
$$+\sum_{\vec{m}''}\Gamma_V s_{\vec{n}-\vec{m}''}[G_3(\vec{m}''\vec{m}\vec{n},t)-G_3(\vec{n}\vec{m}\vec{m}'',t)]+\delta(t)\delta_{\vec{n},0}c_V(1-\delta_{0,\vec{m}}) \ . \tag{2.37}$$

Here $G_3(\vec{n}\vec{m}\vec{m}',t)$ is the density of triplets, i.e., the average number of triplets consisting of the Mössbauer atom at $\vec{n}$, a vacancy at $\vec{m}$, and a second vacancy at $\vec{m}'$. The normalization is

$$\sum_{\vec{m}'}G_3(\vec{n}\vec{m}\vec{m}',t)=(N_V-1)G_2(\vec{n}\vec{m},t) \ . \tag{2.38}$$

The following processes contribute to the change of $G_2$, Eq. (2.37): The first term describes the exchange of sites of the indicated atom-vacancy pair, the second describes the free diffusion of the vacancy without passing the site $\vec{n}$ of the atom. The next term accounts for jumps of the atom with a second vacancy while the first vacancy is fixed at $\vec{m}$. The last term describes the production of the atom at $t=0$, at the origin ($\vec{n}=0$), in the presence of $N_V=c_VN$ homogenously distributed vacancies, where $N$ is the number of lattice sites.

Now we have to formulate an equation for $G_3$ which contains a density function $G_4$ to describe jumps of the atom with a third vacancy. In that manner one gets a system of coupled equations for $G_i$, which describes the complete dynamics of the system from which we have to determine $G_M$.

### 2. Superposition approximation

The small vacancy density $c_V$ allows to cut off the hierarchy of equations after a few steps. Because of $c_V \ll 1$, the average distance between vacancies is large compared to the nearest-neighbor distance. This means especially if one vacancy is located near the Mössbauer atom on the average the others are far away. But strong correlations are present only over a range of a few jump distances and for larger distances they can be neglected.

The roughest approximation is to consider the atom and vacancy completely independent, i.e., to separate the pair density function: $G_2(\vec{n}\vec{m},t)\approx c_VG_M(\vec{n},t)$. Then from Eq. (2.36) we obtain

$$\dot{G}_M(\vec{n},t)+c_V\sum_{\vec{m}''}\Lambda(\vec{n}-\vec{m}'')G_M(\vec{m}'',t)=\delta(t)\delta_{\vec{n},0}\ . \tag{2.39}$$

This equation of motion has the same structure as Eq. (2.6) for the diffusion of the vacancy, only the jump rates for the atom are scaled by $c_V$. Therefore the atomic distribution changes slowly compared with the distribution of vacancies. In Eq. (2.39) the motion of the atom is described by random jumps to empty neighbor sites with jump rates $\Gamma_M=c_V\Gamma_V$; here correlations are neglected.

In order to take into account correlations we only approximate the triplet density function. In the equation of motion (2.37), $G_3(\vec{n}\vec{m}\vec{m}'',t)$ appears in terms describing the exchanges of sites of the atom at $\vec{n}$ with the vacancy at $\vec{m}''$. Because of $c_V \ll 1$ the other vacancy (at $\vec{m}$) is far away on the average, and we neglect its correlations with the atom-vacancy pair at ($\vec{n}\vec{m}''$). Thus we set

$$G_3(\vec{n}\vec{m}\vec{m}'',t)\approx c_VG_2(\vec{n}\vec{m}'',t)\ . \tag{2.40}$$

Then we obtain from Eq. (2.37)

$$\begin{aligned}\dot{G}_2(\vec{n}\vec{m},t)={}&\Gamma_Vs_{\vec{n}-\vec{m}}[G_2(\vec{m}\vec{n},t)-G_2(\vec{n}\vec{m},t)]+(1-\delta_{\vec{n},\vec{m}})\sum_{\vec{m}''}(1-\delta_{\vec{n},\vec{m}''})\Gamma_Vs_{\vec{m}-\vec{m}''}[G_2(\vec{n}\vec{m}'',t)-G_2(\vec{n}\vec{m},t)]\\&+c_V\dot{G}_M(\vec{n},t)-\delta(t)c_V\delta_{\vec{n},0}\delta_{0,\vec{m}}\ .\end{aligned} \tag{2.41}$$

A general solution of this equation can be given with the pair-correlation function $W$, Eq. (2.3), i.e.,

$$\begin{aligned}G_2(\vec{n}\vec{m},t)&=c_V\int_0^t dt'\sum_{\vec{n}',\vec{m}'}W(\vec{n}\vec{m},t-t'|\vec{n}'\vec{m}')\frac{\partial}{\partial t'}G_M(\vec{n}',t')\\&=c_V\int_0^t dt'\sum_{\vec{n}',\vec{m}'}\frac{\partial}{\partial t}W(\vec{n}\vec{m},t-t'|\vec{n}'\vec{m}')G_M(\vec{n}',t')\ .\end{aligned} \tag{2.42}$$

The last equation is obtained by partial integration.

### *3. Jump matrix for the Mössbauer atom*

Substitution of Eq. (2.42) into (2.36) yields for $\dot{G}_M$

$$\dot{G}_M(\vec{n},t)+\sum_{\vec{n}'}\int dt'\,\Phi(\vec{n}-\vec{n}',t-t')\,G_M(\vec{n}',t')=\delta(t)\delta_{\vec{n},0}\ , \tag{2.43}$$

with the matrix

$$\begin{aligned}\Phi(\vec{n}-\vec{n}',t)&=c_V\sum_{\vec{m}}\Gamma_Vs_{\vec{n}-\vec{m}}\sum_{\vec{m}'}[W(\vec{n}\vec{m},t|\vec{n}'\vec{m}')-\dot{W}(\vec{m}\vec{n},t|\vec{n}'\vec{m}')]\\&=c_V\sum_{\vec{m}}\Gamma_Vs_{\vec{n}-\vec{m}}[\dot{T}_M(\vec{n}',t|\vec{n}\vec{m})-\dot{T}_M(\vec{n}',t|\vec{m}\vec{n})]\end{aligned} \tag{2.44}$$

Equation (2.43) has a more general structure than the equations for jump diffusion discussed so far, e.g., Eq. (2.39), since the development in time of all atomic jumps induced by one vacancy is considered. Instead of the coupling matrix $c_V\Lambda(\vec{n})$ describing instantanous jumps, here the integral operator $\Phi(\vec{n}-\vec{n}',t)$ appears, which describes the temporal sequence of the jumps of the atom with one vacancy. The dimension of $\Phi$ is that of a jump rate per unit time and it contains two factors: (i) the characteristic jump rate $\Gamma_M = c_V\Gamma_V$ that is well known from Eq. (2.39), (ii) a term describing the spatial and temporal correlations between the atom and a single vacancy. Because of the symmetry operations (translation and inversion) of the lattice, $\Phi$ depends only on the difference $\pm(\vec{n}-\vec{n}')$ of the starting and end positions of the atom. The relation

$$\sum_{\vec{n}-\vec{n}'} \Phi(\vec{n}-\vec{n}',t) = 0 \tag{2.45}$$

is satisfied, which guarantees the conservation of the number of particles.

Fourier-transformation $t \to \omega$ of Eq. (2.43) yields

$$(-i\omega)\tilde{G}_M(\vec{n},\omega) + \sum_{\vec{n}'} \tilde{\Phi}(\vec{n}-\vec{n}',\omega)\,\tilde{G}_M(\vec{n}',\omega) = \delta_{\vec{n},0} \ . \tag{2.46}$$

Here we have

$$\tilde{\Phi}(\vec{n}-\vec{n}',\omega) = c_V \sum_{\vec{m}} \Gamma_V s_{\vec{n}-\vec{m}} \sum_{\vec{m}'} [(-i\omega)\,\tilde{W}(\vec{n}\,\vec{m},\omega\,|\,\vec{n}'\vec{m}') - (-i\omega)\,\tilde{W}(\vec{m}\,\vec{n},\omega\,|\,\vec{n}'\vec{m}')] \ , \tag{2.47}$$

which is a frequency dependent, generalized (effective) jump matrix, which in general is a complex quantity.

### C. Approximations for the effective jump matrix

#### *1. Instantaneous atom transfer*

The time dependence of the matrix $\Phi(\vec{n}-\vec{n}',t)$ is determined by the time dependence of the distribution function $T_M$ of the Mössbauer atom due to jumps with a single vacancy. Because the vacancy leaves the neighborhood of the atom with large probability already after a few jumps, the time dependence of the atomic distribution and thus of $\Phi$ is restricted to times of the order of magnitude of $\Gamma_V^{-1}$. During this time interval, the vacancy performs relatively many ($\approx Z$) jumps and covers relatively large distances, whereas the atom practically remains at its site because of its much smaller jump rate $\Gamma_M = c_V\Gamma_V$. So for times $t \gg \Gamma_V^{-1}$ it is a good approximation to neglect the time dependence of $\Phi$ and use the stationary limit $t \to \infty$ for the term describing the atomic transfer in the equation of motion (2.43). Thus we obtain from the integral

$$\begin{aligned}\int_0^\infty dt'\,\Phi(\vec{n}-\vec{n}',t-t')\,G_M(\vec{n}',t') \\ \approx \left(\int_0^\infty d\tau\,\Phi(\vec{n}-\vec{n}',\tau)\right) G_M(\vec{n}',t) \ ,\end{aligned} \tag{2.48}$$

where for small $\tau = t - t'$ we replaced $G_M(\vec{n}',t')$ by $G_M(\vec{n}',t)$. A consistent Taylor expansion is not possible here, since the term linear in $\tau$ leads to a divergent integral.[18] Then the equation of motion reads

$$\dot{G}_M(\vec{n},t) + \sum_{\vec{n}'} \Lambda^{\text{eff}}(\vec{n}\,\vec{n}')\,G_M(\vec{n}',t) = \delta(t)\,\delta_{\vec{n},0} \tag{2.49}$$

with the effective jump matrix for the atom

$$\begin{aligned}\Lambda^{\text{eff}}(\vec{n}-\vec{n}') &= \int_0^\infty d\tau\,\Phi(\vec{n}-\vec{n}',\tau) \\ &= \tilde{\Phi}(\vec{n}-\vec{n}',\omega=0) \ ,\end{aligned} \tag{2.50}$$

$\Lambda^{\text{eff}}$ still contains all spatial correlations. It is determined by the total broadening of the atomic distribution caused by a single vacancy. In this limit all jumps between $\vec{n}'$ and $\vec{n}$ contained in $\Lambda^{\text{eff}}$ are considered as happening instantaneously. Such a time-independent approximation for the atomic transfer has already been used by several authors for the description of diffusion via vacancies.[7,8,16,17]

Since in the case of continuum diffusion only the effective displacement of the diffusing atom is important and not its temporal development, we can calculate from $\Lambda^{\text{eff}}$ the diffusion coefficient $D_M^{\text{corr}}$ of the Mössbauer atom. It is defined as the second moment of the jump matrix[19]

$$\begin{aligned}D_M^{\text{corr}} &= -\tfrac{1}{2}\sum_{\vec{1}} (\vec{r}^{\,\vec{1}})^2\,\Lambda^{\text{eff}}(\vec{1}) \\ &= f D_M^{\text{uncorr}} = f c_V D_V \ .\end{aligned} \tag{2.51}$$

Here $f$ is the correlation factor and

$$D_V = -\tfrac{1}{2}\sum_{\vec{1}} (\vec{R}^{\vec{1}})^2\,\Lambda(\vec{1}) = \frac{Zd^2}{6}\Gamma_V$$

is the diffusion coefficient of the vacancy. $D_M^{\text{uncorr}}$ would be the diffusion coefficient of the atom if no correlations were present. $d$ is the nearest-neighbor distance.

### 2. *Expansion of the effective jump matrix with respect to the number of atomic jumps*

In order to calculate the distribution of an atom diffusing via vacancies D. Wolf,[16] and Dibar Ure and Flinn[10] have used numerical integration methods.

We obtain analytical results for the distribution function $G_M$ of the Mössbauer atom by expanding the generalized jump matrix $\tilde{\Phi}(\vec{n}-\vec{n}',\omega)$ with respect to the number of the atomic jumps. We make use of the iteration procedure for $W$ described in Sec. IIA 3.

In a zero-order approximation we calculate $\tilde{\Phi}_0(\vec{n}-\vec{n}',\omega)$ with the help of $\tilde{W}_0$ from Eq. (2.34) and obtain

$$\tilde{\Phi}_0(\vec{n}-\vec{n}',\omega)=c_V\left(\sum_{\vec{m}}\Gamma_V s_{\vec{n}-\vec{m}}\delta_{\vec{n},\vec{n}'}\sum_{\vec{m}'}(-i\omega)\tilde{F}_{\vec{n}}(\vec{m},\omega|\vec{m}')-\Gamma_V s_{\vec{n}-\vec{n}'}\sum_{\vec{m}'}(-i\omega)\tilde{F}_{\vec{n}'}(\vec{n},\omega|\vec{m}')\right| \quad . \tag{2.52}$$

$\tilde{\Phi}_0$ describes the atomic transfer from $\vec{n}'$ to $\vec{n}$ by one jump with a vacancy. We can express $\tilde{\Phi}_0$ by the Green's function $\tilde{G}_V(\vec{n},\omega)$ of the vacancy which can be calculated numerically.[12,20] Using Eqs. (2.11), (2.12), and (2.24) we get

$$\tilde{\Phi}_0(\vec{n}-\vec{n}',\omega)=c_V\Lambda(\vec{n}-\vec{n}')[1-\tilde{\alpha}(\omega)] \quad , \tag{2.53}$$

with $\Lambda(\vec{n}-\vec{n}')$ given by Eq. (2.7) and $\tilde{\alpha}(\omega)$ by Eq. (2.25). The structure of the matrix $\tilde{\Phi}_0$ is the same as that of the jump matrix $\Lambda$, i.e., it includes nearest-neighbor jumps only. The jump rates of the atom are proportional to the vacancy density $c_V$. The factor $[1-\tilde{\alpha}(\omega)]$ is due to the fact that only such vacancies contribute to $\tilde{\Phi}_0$ which induce a single (uncorrelated) jump of the atom.

As a next step we use $\tilde{W}_1$ from Eq. (2.35) to compute $\tilde{\Phi}_1$, and as a function of $\tilde{G}_V$ we eventually obtain

$$\begin{aligned}\tilde{\Phi}_1(\vec{n}-\vec{n}',\omega)&=c_V\Lambda(\vec{n}-\vec{n}')[1-\tilde{\alpha}(\omega)]+c_V[1-\tilde{\alpha}(\omega)]\{\tilde{\alpha}(\omega)\Gamma_V s_{\vec{n}'-\vec{n}''}-a(\vec{n}-\vec{n}')\Gamma_V^2\\&\qquad\times[\tilde{G}_V(\vec{n}-\vec{n}',\omega)-\tilde{\alpha}(\omega)\tilde{G}_V(N_1,\omega)]\}\\&=\tilde{\Phi}_0(\vec{n}-\vec{n}',\omega)+\tilde{\Phi}^{(1)}(\vec{n}-\vec{n}',\omega) \quad .\end{aligned} \tag{2.54}$$

The matrix $\tilde{\Phi}_1$ contains two jumps of the atom with the same vacancy. The additional term $\tilde{\Phi}^{(1)}$ in Eq. (2.54) describes jump rates to sites, which the atom is able to reach with exactly two jumps. Here we have

$$\begin{aligned}a(\vec{n}-\vec{n}')&=\sum_{\vec{m}}s_{\vec{n}-\vec{m}}s_{\vec{m}-\vec{n}'}\\&=\sum_i a^{(i)}s^{(i)}(\vec{n}-\vec{n}') \quad ,\end{aligned} \tag{2.55}$$

which is the number of lattice sites which are mutual nearest neighbors of $\vec{n}$ and $\vec{n}'$. We have decomposed it into contributions from different coordination shells $i$: $a^{(i)}$ is the number of nearest-neighbor sites of $\vec{n}$ and $\vec{n}'$ if $\vec{n}$ is in the $i$th shell with respect to $\vec{n}'$. The functions $s^{(i)}(\vec{n}-\vec{n}')$ describe the coordination of $\vec{n}$ and $\vec{n}'$, i.e.,

$$s^{(i)}(\vec{n}-\vec{n}')=\begin{cases}1, & \text{if } \vec{n} \text{ and } \vec{n}' \text{ are } i\text{th neighbors}\\ 0, & \text{otherwise}\end{cases} \quad ,$$

e.g., $s^{(0)}(\vec{n}-\vec{n}')=\delta_{\vec{n},\vec{n}'}$ and $a^{(0)}=Z$. $s^{(1)}(\vec{n}-\vec{n}')$ is identical with $s_{\vec{n}'-\vec{n}''}$ from Eq. (2.4). The terms described by $a(\vec{n}-\vec{n}')$ have a longer than nearest-neighbor range, e.g., as far as the 5th neighbor in bcc lattices.[12]

If one includes one more atomic jump in the calculation of $\tilde{\Phi}$ the jump probabilities to all sites which are reached by the previous approximation are changed and the range of $\tilde{\Phi}$ is extended by one more jump distance. The corrections to $\tilde{\Phi}$ decrease with the number $\mu$ of jumps considered proportional to $[\tilde{\alpha}(\omega)]^{\mu+1}$. The condition of particle conservation, Eq. (2.45), is fulfilled for any order of iteration, i.e., $\sum_{\vec{n}-\vec{n}'}\tilde{\Phi}_\mu(\vec{n}-\vec{n}',\omega)=0$.

## III. SHAPE OF THE MÖSSBAUER LINE

### A. General result for the line shape

According to Eq. (1.1) the scattering function is given by the Fourier transform of the Green's function of the Mössbauer atom, i.e.,

$$\begin{aligned}S(\vec{k},\omega)&=\int_0^\infty dt\,\tfrac{1}{4}\gamma e^{-\gamma t/2}(e^{-i\omega t}+e^{i\omega t})\\&\qquad\times\sum_{\vec{n}}e^{-i\vec{k}\cdot\vec{R}^{\vec{n}}}G_M(\vec{n},t)\\&=\tfrac{1}{4}\gamma[\hat{G}_M(\vec{k},-\omega+i\tfrac{1}{2}\gamma)+\hat{G}_M(\vec{k},\omega+\tfrac{1}{2}\gamma)]\end{aligned} \tag{3.1}$$

Equation (2.43) yields

$$\hat{G}_M(\vec{k}, \omega) = [-i\omega + \hat{\Phi}(\vec{k}, \omega)]^{-1} \ , \tag{3.2}$$

with a complex $\hat{\Phi}(\vec{k}, \omega)$. It can be shown[12] that the real part of $\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma)$, $\mathrm{Re}\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma)$ is an even function of $\omega$ while the imaginary part, $\mathrm{Im}\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma)$ is odd, i.e.,

$$\mathrm{Re}\hat{\Phi}(\vec{k}, \omega + i\tfrac{1}{2}\gamma) = \mathrm{Re}\hat{\Phi}(\vec{k}, -\omega + i\tfrac{1}{2}\gamma) \ ;$$

$$\mathrm{Im}\hat{\Phi}(\vec{k}, \omega + i\tfrac{1}{2}\gamma) = -\mathrm{Im}\hat{\Phi}(\vec{k}, -\omega + i\tfrac{1}{2}\gamma) \ . \tag{3.3}$$

After some rearrangements we thus obtain for the scattering function

$$S(\vec{k}, \omega) = \frac{1}{2}\gamma \frac{\frac{1}{2}\gamma + \mathrm{Re}\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma)}{[\frac{1}{2}\gamma + \mathrm{Re}\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma)]^2 + [\mathrm{Im}\hat{\Phi}(\vec{k}, \omega + i\frac{1}{2}\gamma) - \omega]^2} \tag{3.4}$$

Because of the frequency-dependent jump matrix the Mössbauer line is, in general, not a Lorenzian. To calculate the line shape we need the frequency-dependent vacancy Green's function $\tilde{G}_V(\vec{m}, \omega)$, which is discussed in detail in Ref. 12. In the Appendix we show that the $\omega$ dependence of $\hat{\Phi}$ has no measurable effect in the case of self-diffusion, i.e., temporal correlation can not be detected. So it is sufficient to use the frequency-independent jump matrix (encounter model, Sec. II.C 1). Of course for jump frequencies $\Gamma_M = c_V\Gamma_V$ small compared to the natural line width $\gamma$, i.e., at low temperatures, Eq. (3.4) simplifies to the scattering function of a Mössbauer atom bounded at a single site in the lattice, i.e.,

$$S(\vec{k}, \omega) = (\gamma^2/4)(\gamma^2/4 + \omega^2)^{-1} \ .$$

### B. Diffusion broadening (frequency-independent jump matrix)

In the case of the instantaneous transfer of the atom we get from Eq. (2.49)

$$\hat{G}_M(\vec{k}, \omega) = [-i\omega + \tilde{\Lambda}^{\mathrm{eff}}(\vec{k})]^{-1} \ , \tag{3.5}$$

and the scattering function reads

$$S(\vec{k}, \omega) = \frac{\gamma}{2} \frac{\frac{1}{2}\gamma + \tilde{\Lambda}^{\mathrm{eff}}(\vec{k})}{[\frac{1}{2}\gamma + \tilde{\Lambda}^{\mathrm{eff}}(\vec{k})]^2 + \omega^2} \ . \tag{3.6}$$

Here $S(\vec{k}, \omega)$ describes a Lorenzian spectral line with total width $\gamma + 2\tilde{\Lambda}^{\mathrm{eff}}(\vec{k})$. The broadening due to diffusion is given by $2\tilde{\Lambda}^{\mathrm{eff}}(\vec{k})$.

#### *1. Zero-order approximation*

The zero-order approximation $\tilde{\Phi}_0$ for the jump matrix, Eq. (2.53), yields for the diffusion broadening

$$2\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k}) = 2\tilde{\Phi}_0(\vec{k}, \omega = 0) = 2c_V(1-R)\tilde{\Lambda}(\vec{k}) \ . \tag{3.7}$$

$R$ is given by Eq. (2.26) and $\tilde{\Lambda}(\vec{k})$ is given by Eq. (2.10). The broadening (3.7) consists of three characteristic factors. The jump rate of the Mössbauer atom $\Gamma_M = c_V\Gamma_V$ determines the order of magnitude of the broadening, and thus the possibility of detecting the diffusional motion in the spectrum. The factor $\tilde{\Lambda}(\vec{k})\Gamma_V^{-1}$ determines the anisotropy of the broadening, i.e., the dependence of the width on the direction of $\gamma$-ray emission relative to the lattice axis. In $\hat{\Phi}_0(\vec{k}, \omega = 0)$ we only consider one jump of the atom with a single vacancy. Thus the $\vec{k}$ dependence is determined by the geometry of the atomic jumps to the nearest neighbors. The third factor $1-R$ is the reduction factor due to the neglect of further jumps of the atom with each vacancy. Calculating the second moment of $\tilde{\Lambda}_0{}^{\mathrm{eff}}$ according to Eq. (2.51) we find that $1-R$ is the value of the correlation factor in this zero-order approximation. In this approximation the effect of correlations only consists in scaling the uncorrelated jump rates $\Gamma_M = c_V\Gamma_V$ by the correlation factor $f$. Numerical values of $1-R$ and $f$ for cubic lattices are listed in Table I. We see that $1-R$ is a good approximation for the correlation factor, deviations are largest for the fcc-lattice by about 5%.

The anisotropy of the broadening is demonstrated in Figure 1. It shows the values of $2\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\Gamma_M^{-1}$ for different orientations of the $\vec{k}$ vector in a stereographic projection. We have plotted contour lines for a bcc lattice with the absolute value of the wave-vector $|\vec{k}| = 7.3$ Å$^{-1}$ and the lattice constant $a = 2.86$ Å. These values apply to diffusion of $^{57}$Fe in $\alpha$-iron. The width varies between $23\Gamma_M$ for $\vec{k}$ approximately in the ⟨311⟩ direction and $1.1\Gamma_M$ in the ⟨111⟩ direction.

TABLE I. Correlation factor in zero-order approximation.

| Lattice type | sc | bcc | fcc |
|---|---|---|---|
| $1-R$ | 0.6595 | 0.7178 | 0.7437 |
| $f$ | 0.6531 | 0.7272 | 0.7815 |

### 2. *First-order approximation*

From Eq. (2.54) we obtain the broadening in first-order approximation, i.e.,

$$2\tilde{\Lambda}_1{}^{\mathrm{eff}}(\vec{k})=2c_V(1-R)\tilde{\Lambda}(\vec{k})+2c_V(1-R)\sum_{\vec{n}'-\vec{n}''}\cos\vec{k}\cdot\vec{R}^{\vec{n}'-\vec{n}''}\{R\Gamma_V s_{\vec{n}'-\vec{n}''}-a(\vec{n}-\vec{n}')\times\Gamma_V^2[g_V(\vec{n}-\vec{n}')-Rg_V(N_1)]\}=2\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})+2\tilde{\Lambda}^{(1)\mathrm{eff}}(\vec{k}) \qquad (3.8)$$

The correction term $\tilde{\Lambda}^{(1)\mathrm{eff}}(\vec{k})$ changes the $\vec{k}$ dependence of the zero-order approximation. The influence of correlated diffusion can no longer be described by a scaling factor independent of $\vec{k}$, but a specific spatial effect of the correlated jumps enters. The $\vec{k}$ dependence of $\tilde{\Lambda}_1{}^{\mathrm{eff}}(\vec{k})$ is determined by the geometry of lattice sites which can be reached by two atomic jumps.

In Fig. 2, $2\tilde{\Lambda}_1{}^{\mathrm{eff}}(\vec{k})\Gamma_M^{-1}$ is plotted for parameters applying to $^{57}$Fe isotopes diffusing in $\alpha$-iron. The orientation dependence of the broadening is changed little compared to the zero-order approximation, but the extrema are smoothed out; for example in the

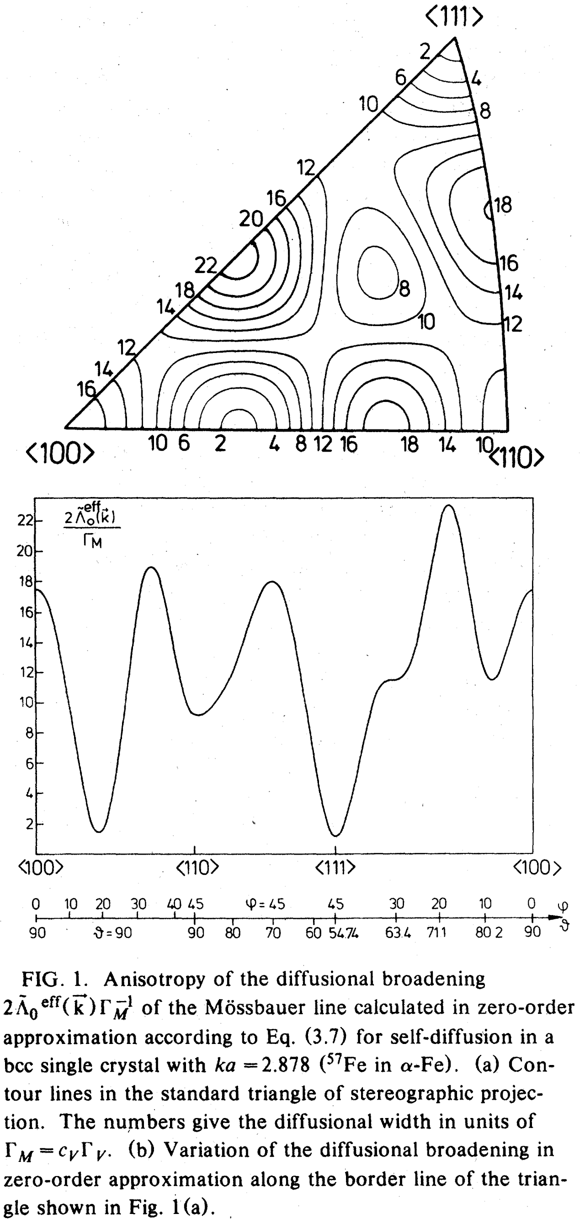

FIG. 1. Anisotropy of the diffusional broadening $2\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\Gamma_M^{-1}$ of the Mössbauer line calculated in zero-order approximation according to Eq. (3.7) for self-diffusion in a bcc single crystal with $ka=2.878$ ($^{57}$Fe in $\alpha$-Fe). (a) Contour lines in the standard triangle of stereographic projection. The numbers give the diffusional width in units of $\Gamma_M=c_V\Gamma_V$. (b) Variation of the diffusional broadening in zero-order approximation along the border line of the triangle shown in Fig. 1(a).

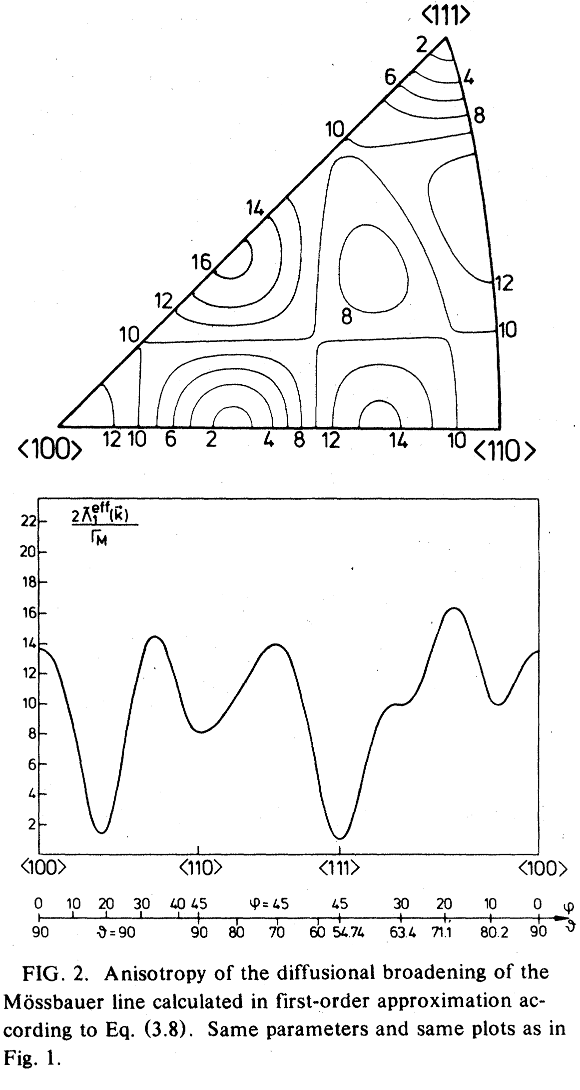

FIG. 2. Anisotropy of the diffusional broadening of the Mössbauer line calculated in first-order approximation according to Eq. (3.8). Same parameters and same plots as in Fig. 1.

$\langle 311\rangle$ direction we find $2\tilde{\Lambda}_1{}^{\text{eff}}(\vec{k}) \approx 16\Gamma_M$, i.e., a reduction of about 30%. However, there remains a remarkable difference between the maximum value close to the $\langle 311\rangle$ direction and the minimum in the $\langle 111\rangle$ direction.

We do not expect that further approximations will modify the results essentially, because the corrections are of the order of $R^3$ which is small since $R$ is about 0.3.

## IV. SUMMARY AND DISCUSSION

We have analytically calculated the shape of the Mössbauer line taking into account the diffusion of substitutional Mössbauer atoms via vacancies. We have only considered self-diffusion in single crystals. The line shape is determined by an effective jump frequency matrix which we have derived using a microscopic description of the motion of an atom via vacancies, and taking into account spatial and temporal correlations of the jumps. We have shown that for self-diffusion, temporal correlations are not detectable. Thus the Mössbauer line is only broadened which can be measured at high temperatures when the atomic jump rate is at least of the same order of magnitude as the natural line width. The anisotropy of the broadening due to the discrete jump distances in a lattice is modified by the spatial correlations of the jumps.

We have calculated the diffusion broadening in two approximations. In our zero-order approximation in which we taken into account one atomic jump with each vacancy, the anisotropy is determined by the geometry of the nearest neighbors just as for an uncorrelated diffusing vacancy. In this approximation the effect of correlations only consists in a scaling of the atomic jump rate by the macroscopic correlation factor. In the first-order approximation, in which two atomic jumps with one vacancy are considered, the anisotropy is changed and the particular geometry of the correlated atomic jumps enters explicitly. A pure scaling of the atomic jump rates by a $\vec{k}$-independent factor is no longer possible even though the general features of the aniotropy remain the same (see Figs. 1 and 2). We expect the same to be true for any further approximation.

Our results are in general agreement with the numerical results obtained by Dibar-Ure and Flinn.[10] They simulated the atomic jump diffusion in sc and bcc lattices numerically and found that the main effect of the correlation for the line broadening is a reduction of the atomic jump rates by the Bardeen-Herring correlation factor. But they also found deviations from the nearest-neighbor anisotropy in some $\vec{k}$ directions. Our analytical results in general give larger deviations. For example, Dibar-Ure and Flinn found deviations of about 10% in the $\langle 7\,10\,0\rangle$ direction where we obtain deviations of about 20%. In the $\langle 310\rangle$ direction, we find in agreement with these authors, only small deviations (about 4%). A more detailed comparison with these numerical results is not possible because the authors give numbers only for a few $\vec{k}$ directions. Wolf[11] has recently specialized his work on the influence of diffusion on NMR to Mössbauer spectroscopy, producing essentially the same results as ours. He also finds deviations from the simple scaling of the atomic jump rates by the correlation factor which are due to the specific way in which the jumps of a Mössbauer atom with a single vacancy ("encounter") enter the linewidth. In earlier papers[16] he calculated the distribution function of an atom after such an encounter. Our iteration procedure gives a prescription on how to calculate this distribution up to a certain order in the return probability $R$ (see Sec. II A).

The anisotropy of the diffusion broadening can only be measured in experiments with single crystals. However, so far only polycrystalline or powder measurements have been reported.[2–6] To compare our theoretical results with these experimental data we have to average the scattering function over the orientations of the crystallites. The technique is described, e.g., by Dibar-Ure and Flinn.[9] They performed the averaging for a nearest-neighbor jump model. A rough estimate for the averaged $\langle S(\vec{k},\omega)\rangle$ can be obtained by using the averaged width $\langle\tilde{\Lambda}^{\text{eff}}(\vec{k})\rangle$. This approximation can be improved by a cumulant expansion.[21] According to Eq. (3.1), $\langle S(\vec{k},\omega)\rangle$ is determined by the averaged Green's function $\langle\hat{G}_M(\vec{k},\pm\omega+i\frac{1}{2}\gamma)\rangle$. The first-order cumulant approximation reads

$$\langle\hat{G}_M(\vec{k},\omega)\rangle = \left[-i\omega+\langle\tilde{\Lambda}^{\text{eff}}(\vec{k})\rangle - \left\langle\delta\tilde{\Lambda}(\vec{k})\frac{1}{-i\omega+\langle\tilde{\Lambda}^{\text{eff}}(\vec{k})\rangle}\delta\tilde{\Lambda}(\vec{k})\right\rangle\right]^{-1} \tag{4.1}$$

with

$$\delta\tilde{\Lambda}(\vec{k})=\tilde{\Lambda}^{\text{eff}}(\vec{k})-\langle\tilde{\Lambda}^{\text{eff}}(\vec{k})\rangle\ .$$

We will estimate the polycrystalline broadening by averaging the effective jump matrix. With

$$\langle\cos\vec{k}\cdot\vec{R}^{\vec{n}}\rangle=\frac{\sin|\vec{k}||\vec{R}^{\vec{n}}|}{|\vec{k}||\vec{R}^{\vec{n}}|}\ ,$$

we obtain from the zero-order approximation, Eq. (3.7),

$$\langle\tilde{\Lambda}_0{}^{\text{eff}}(\vec{k})\rangle=\Gamma_M Z(1-R)\left[1-\frac{\sin kd}{kd}\right]\ . \tag{4.2}$$

For Mössbauer spectroscopy, the product $kd$ is always much larger than unity (e.g., $kd\approx 21$ for $^{57}$Fe in $\alpha$-Fe), so we obtain from Eq. (4.2)

$$\langle\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\rangle \cong \Gamma_M Z(1-R) \quad . \tag{4.3}$$

Following Wolf[11] one can interprete this as the inverse of an effective mean residence time for a Mössbauer atom: $(\Gamma_M Z)^{-1}$ would be the mean residence time for an uncorrelated random walk and $(1-R)^{-1}$ is the mean number of jumps of an atom during an encounter with a vacancy (see Sec. II.A).

The first-order approximation, Eq. (3.8), yields

$$\langle\tilde{\Lambda}_1{}^{\mathrm{eff}}(\vec{k})\rangle \cong \Gamma_M Z(1-R)\left[1-\frac{1+R}{Z}\right] \quad . \tag{4.4}$$

The broadening $2\langle\Lambda_1{}^{\mathrm{eff}}(\vec{k})\rangle$ is always smaller than $2\langle\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\rangle$. The additional factor $(1-1+R/Z)<1$ accounts for the fact that in this approximation the Mössbauer atom has a finite probability, given by $(1+R)/Z$, to return to its original site. Similar arguments have been presented by Knauer.[7] The reduction depends on the type of lattice, it is 22.3% in sc, 16.3% in bcc and 10.5% in fcc lattices. Note that the scaling factor $(1-R)[1-(1+R)/Z]$ in Eq. (4.4) is not identical with the correlation factor in first order [whereas $(1-R)$ is for the zero-order approximation]. The respective values are listed in Table II.

TABLE II. Scaling of $\langle\tilde{\Lambda}^{\mathrm{eff}}(\vec{k})\rangle$ and correlation factor in first-order approximation.

| Lattice Type | sc | bcc | fcc |
|---|---|---|---|
| first-order approximation for $f$ | 0.6073 | 0.6936 | 0.7518 |
| $(1-R)[1-(1+R)/Z]$ | 0.4735 | 0.5828 | 0.6549 |

For the interpretation of experimental data of line broadening[2-6] mostly the diffusion model of Singwi and Sjölander[1] has been applied using a jump frequency scaled with the correlation factor. The polycrystalline width was approximated by the averaged width. The values of the width calculated with this model using parameters obtained from tracer experiments were a factor of 2 larger than the measured width for diffusion of $^{57}$Fe in Fe,[5] Cu,[2] and Au.[3] This discrepancy has stimulated a lot of discussions (see, e.g., the review of Janot[22]). Dibar-Ure and Flinn[7] have shown that proper averaging of the scattering function instead of the width leads to smaller values for the polycrystalline width, e.g., for $^{57}$Fe in iron by a factor of 0.85. Taken into account properly, the correlated motion yields a further reduction of the width as we have shown above and was also found by Wolf[11] and Knauer[7].

A reason for the remaining discrepancies may be the disturbance of vacancy jumps in the neighborhood of substitutional Mössbauer atoms like $^{57}$Fe in Cu and Au. Such disturbances have beeen considered, e.g., by Krivoglaz and Repetsky[8] who have shown that due to local motion of the vacancy Mössbauer atom pair the intensity of the Mössbauer line decreases. In our approach, these disturbances can be included by considering changed vacancy jump rates in the equation of motion for the correlation function $W$. We are currently considering this.

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## APPENDIX

### A. Change of the Mössbauer line shape due to the frequency dependence of the jump matrix

In this Appendix we will discuss the effect of the frequency dependent jump matrix on the scattering function, especially considering consequences for the shape of the detectable Mössbauer spectrum. For simplicity, we use the zero-order approximation $\hat{\Phi}_o(\vec{k},\omega)$. Then the scattering function reads

$$S(\vec{k},\omega)=\frac{\gamma}{2}\,\frac{\frac{1}{2}\gamma+\mathrm{Re}\hat{\Phi}_0(\vec{k},\omega+i\frac{1}{2}\gamma)}{[\frac{1}{2}\gamma+\mathrm{Re}\hat{\Phi}_0(\vec{k},\omega+i\frac{1}{2}\gamma)]^2+[\mathrm{Im}\hat{\Phi}_0(\vec{k},\omega+i\frac{1}{2}\gamma)-\omega]^2} \tag{A1}$$

From Eq. (2.53) we obtain for the real and imaginary part of $\hat{\Phi}_0(\vec{k},\omega+i\frac{1}{2}\gamma)$

$$\mathrm{Re}\Phi_o(\vec{k},\omega+i\tfrac{1}{2}\gamma)=c_V\tilde{\Lambda}(\vec{k})[1-\mathrm{Re}\tilde{\alpha}(\omega+i\tfrac{1}{2}\gamma)]\,;\;\;\mathrm{Im}\hat{\Phi}_0(\vec{k},\omega+i\tfrac{1}{2}\gamma)=-c_V\tilde{\Lambda}(\vec{k})\mathrm{Im}\tilde{\alpha}(\omega+i\tfrac{1}{2}\gamma)\quad , \tag{A2}$$

where $\tilde{\alpha}(\omega+i\frac{1}{2}\gamma)$ is given in Eq. (2.25) in terms of the vacancy Green's function. Thus we have

$$\mathrm{Re}\tilde{\alpha}(\omega+i\tfrac{1}{2}\gamma)=\frac{\mathrm{Re}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)\mathrm{Re}\tilde{G}_V(N_1,\omega+i\frac{1}{2}\gamma)-\mathrm{Im}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)\mathrm{Im}\tilde{G}_V(N_1,\omega+i\frac{1}{2}\gamma)}{[\mathrm{Re}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)]^2+[\mathrm{Im}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)]^2}\ ,$$

$$\mathrm{Im}\tilde{\alpha}(\omega+i\tfrac{1}{2}\gamma)=\frac{\mathrm{Re}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)\mathrm{Im}\tilde{G}_V(N_1,\omega+i\frac{1}{2}\gamma)-\mathrm{Re}\tilde{G}_V(N_1,\omega+i\frac{1}{2}\gamma)\mathrm{Im}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)}{[\mathrm{Re}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)]^2+[\mathrm{Im}\tilde{G}_V(0,\omega+i\frac{1}{2}\gamma)]^2}\ . \qquad \text{(A3)}$$

Since the diffusion broadening is visible only if it is at least of the same order of magnitude as the natural linewidth $\gamma$ we can neglect the natural linewidth in the following discussion. Frequencies $\omega$ smaller than about $0.1(\frac{1}{2}\gamma)$ are not detectable with Mössbauer spectroscopy, and the intensity of the line decreases quickly for high frequencies $\omega \gtrsim 10^2 c_V\Gamma_V >> \mathrm{Re}\hat{\Phi}_0$. Thus we restrict our discussion to the frequency range

$$0.1(\tfrac{1}{2}\gamma) < \omega < 10^2 c_V\Gamma_V \quad \mathit{or} \quad 0.1\frac{\gamma}{2\Gamma_V} < \frac{\omega}{\Gamma_V} < 10^2 c_V\ . \qquad \text{(A4)}$$

Because we have $c_V < 10^{-4}$, the frequency ratio $\omega/\Gamma_V$ in Eq. (A4) always is much smaller than unity. For $\omega/\Gamma_V << 1$ we are able to calculate the frequency dependence of $\hat{\Phi}_0(\vec{k},\omega)$ explicitly with the help of the frequency-dependent vacancy Green's function $\tilde{G}_V(\vec{m},\omega)$ for low frequencies which is discussed in detail in our earlier report.[12] Here we only list the important results. For $\omega/\Gamma_V << 1$ one finds, neglecting terms of higher order than $\omega^{1/2}$,

$$\mathrm{Re}\tilde{G}_V(\vec{m},\omega)=g_V(\vec{m})-\frac{a_0}{\Gamma_V^{3/2}}\omega^{1/2}\ ;$$

$$\mathrm{Im}\tilde{G}_V(\vec{m},\omega)=\frac{a_0}{\Gamma_V^{3/2}}\omega^{1/2} \qquad \text{(A5)}$$

$a_0$ is a constant depending on the lattice structure

$$a_0=(2)^{1/2}\pi^2/V_B(Zd^2/6)^{3/2}\ .$$

Taking into account only terms of the order of $(\omega/\Gamma_V)^{1/2} << 1$ we obtain from Eqs. (A3) (with $\gamma=0$) the following frequency dependence for $\hat{\Phi}_0(\vec{k},\omega)$:

$$\mathrm{Re}\hat{\Phi}_0(\vec{k},\omega)=\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\left[1+Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2}+O(\omega)\right]\ , \qquad \text{(A6)}$$

$$\mathrm{Im}\hat{\Phi}_0(\vec{k},\omega)=-\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2}+O(\omega)\ ,$$

with $\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})=c_V(1-R)\tilde{\Lambda}(\vec{k})$. This yields for the scattering function

$$S(\vec{k},\omega)=\frac{\gamma}{2}\,\frac{\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})\left[1+Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2}\right]}{\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})^2\left[1+Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2}\right]^2+\left[\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2}-\omega\right]^2}\ . \qquad \text{(A7)}$$

This scattering function does generally not describe a Lorenzian spectral line. Especially for very small frequencies, $\omega/\Gamma_V << 1$, $S(\vec{k},\omega)$ becomes

$$S(\vec{k},\omega)\sim\tfrac{1}{2}\gamma\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})^{-1}[1-Z(1-R)a_0(\omega/\Gamma_V)^{1/2}]\ . \qquad \text{(A8)}$$

However, this decrease proportional to $\omega^{1/2}$ near $\omega\approx 0$ cannot be detected in Mössbauer experiments as we will show now. The $\omega^{1/2}$ terms in (A7) can be neglected if the following conditions are fulfilled:

(i) $Z(1-R)a_0(\omega/\Gamma_V)^{1/2} << 1$

and (A9)

(ii) $\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})Z(1-R)a_0\left(\frac{\omega}{\Gamma_V}\right)^{1/2} << \omega$

Therefore $\omega$ must be limited to

$$\left(\frac{\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})}{\Gamma_V}Z(1-R)a_0\right)^2\Gamma_V << \omega << \frac{\Gamma_V}{[Z(1-R)a_0]^2} \qquad \text{(A10)}$$

As a numerical example we consider a bcc lattice for which we have $a_0=(2)^{1/2}/16\pi$ and the maximum value of $\tilde{\Lambda}_0{}^{\mathrm{eff}}(\vec{k})$ is $16\Gamma_M(1-R)$ with $\Gamma_M=c_V\Gamma_V$. Thus we obtain

$$4c_V\Gamma_M << \omega << 36\Gamma_V\ .$$

This frequency range includes the interval given in

Eq. (A4), if we consider that $\Gamma_M = c_V \Gamma_V$ certainly is less than $10(\frac{1}{2}\gamma)$ and $c_V < 10^{-4}$. The limits do not change essentially for other cubic lattices. Thus the $\omega$ dependence of the jump matrix $\hat{\Phi}_0(\vec{k}, \omega)$ can be neglected in the scattering function in the frequency interval relevant for Mössbauer spectroscopy. This is also valid for other approximations of the jump matrix. So for self-diffusion of Mössbauer atoms via vacancies the influence of the correlated atomic motion consists in broadening of the Mössbauer line, which can be calculated analytically as described in Sec. III. B.

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